

## TECHNICAL MEMORADUM

### Technical Support for Development of a Permitting Framework to Address the Vacatur of the NPDES Vessel Exclusion

**Contract #** EP-C-05-066

**Task Order #** 0004, **Modification #** 0001

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**Subject:** Total Residual Chlorine Test Methods

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### Total Residual Chlorine

#### Summary of Findings:

There are six different testing procedures for analysis of total residual chlorine that are approved by EPA at 40 CFR 136.3. (There are no drinking water standards for total residual chlorine, only for chlorite.) Based on a review of these procedures, **SM4500-Cl G** (DPD Colorimetric Method) appears to be the most appropriate method for analysis of cruise ship wastewater. SM4500-Cl G is the method that ADEC/USCG uses for compliance monitoring and the method ERG used for field measurements during EPA's sampling program.

SM4500-Cl G is the only method that meets all of the following criteria:

- EPA-approved test method at 40 CFR 136.3.
- Applicability to wastewaters with high organic matter.
- Applicability to polluted wastewater.
- Level of sensitivity of 0.010 mg/L, under ideal conditions.

None of the test methods purport a level of sensitivity less than 0.010 mg/L, or of 0.010 mg/L or less under non-ideal conditions.

The following are excerpts from *Standard Methods for the Examination of Water and Wastewater*, 19<sup>th</sup> Edition, 1995:

#### 4500-Cl A CHLORINE (RESIDUAL)

##### 3. Selection of Method

###### a. Natural and treated waters

“The amperometric titration method (D) is a standard of comparison for the determination of free or combined chlorine... A low-level amperometric titration procedure (E) has been added to determine total chlorine at levels below 0.2 mg/L. This method is recommended only when quantification of such low residuals is necessary.... The DPD methods (Methods F and G) are operationally simpler for determining free chlorine than the amperometric titration.”

###### b. Wastewaters

“...For total chlorine in samples containing significant amounts of organic matter, use either the DPD methods (F and G), amperometric, or iodometric back titration method (C) to prevent contact between the full concentration of liberated iodine and the sample....

The DPD titrimetric and colorimetric methods (F and G, respectively) are applicable to determining total chlorine in polluted waters.... Because all methods for total chlorine depend on the stoichiometric production of iodine, water containing iodine-reducing substances may not be analyzed accurately by these methods, especially where iodine remains in solution for a significant time. This problem occurs in Methods B and D. The back titration procedure (C) and Methods F and G cause immediate reaction of the iodine generated so that it has little chance to react with other iodine-reducing substances.”

#### 4500-Cl B Iodometric Method I

“1.c. Minimum detectable concentration: The minimum detectable concentration approximates 0.040 mg Cl as Cl<sub>2</sub>/L if 0.01N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> is used with a 1000-mL sample. Concentrations below 1 mg/L cannot be determined accurately by the starch-iodide end point used in this method. Lower concentrations can be measured with the amperometric end point in Methods C and D.” (EPA’s Engineering Analysis Division, Sample Control Center (SCC) interpreted this paragraph to mean the sensitivity of the method is 1 mg/L.)

See 4500-Cl A, paragraph 3.b regarding problems with this method for water containing iodine-reducing substances.

#### 4500-Cl C Iodometric Method II (amperometric end-point detection)

See 4500-Cl B, paragraph 1.c. (SCC interpreted this paragraph to mean the sensitivity of the method is <1 mg/L.)

“1.b. Interference: ...An unusually high content of organic matter may cause some uncertainty in the end point.”

#### 4500-Cl D Amperometric Titration Method

See 4500-ClB, paragraph 1.c. (SCC interpreted this paragraph to mean the sensitivity of the method is <1 mg/L.)

See 4500-Cl A, paragraph 3.b regarding problems with this method for waster containing iodine-reducing substances.

#### 4500-Cl E Low-Level Amperometric Titration Method

“1. General Discussion: Detection and quantification of chlorine residuals below 0.2 mg/L require special modifications to the amperometric titration procedure. With these modifications, chlorine concentrations at the 0.010 mg/L level can be measured.”

Problems with Method 4500-Cl D also apply to this method.

#### 4500-Cl F DPD Ferrous Titrimetric Method

“1.b. pH control: For accurate results careful pH control is essential.” Maintaining proper pH of 6.2 to 6.5 in the field may be difficult.

“1.e. Minimum detectable concentration: Approximately 0.018 mg Cl as Cl<sub>2</sub>/L. This detection limit is achievable under ideal conditions; normal working detection limits typically are higher.”

#### 4500-Cl G DPD Colormetric Method

“1.c. Minimum detectable concentration: Approximately 0.010 mg Cl as Cl<sub>2</sub>/L. This detection limit is achievable under ideal conditions; normal working detection limits typically are higher.”

Below are excerpts from *EPA's Method for Chemical Analysis of Water and Wastes, 1983*. Note that per EPA's Final Methods Update Rule (72 FR 11200), these methods are no longer approved for analysis of total residual chlorine.

Method 330.1 (comparable to SM4500-Cl D)

"1.1 The amperometric titration method is applicable to all types of waters and wastes that do not contain a substantial amount of organic matter." (No discussion of detection limits.)

Method 330.2 (comparable to SM4500-Cl C)

"1.1 The iodometric back titration method is applicable to all types of waters but is primarily used for wastewater because it eliminates any contact between the full concentration of liberated iodine and the wastewater." (No discussion of detection limits.)

Method 330.3 (comparable to SM4500-Cl B)

"1.1 The iodometric titration method is applicable to natural and treated waters at concentrations greater than 0.1 mg/L." (No discussion of detection limits.)

Method 330.4 (comparable to SM4500-Cl F)

"1.1 The N,N-diethyl-p-phenylene diamine (DPD) – ferrous ammonium sulfate (FAS) titration method is applicable to natural and treated waters at concentrations above 0.1 mg/L Cl." (No discussion of detection limits.)

Method 330.5 (comparable to SM4500-G)

"1.1 The DPD-Colorimetric method is applicable to natural and treated waters at concentrations from 0.2 to 4 mg/L." (No discussion of detection limits.)

## USCG/ADEC Cruise Ship Compliance Testing

The following is an excerpt from:

Northwest CruiseShip Association, Discharge of Effluents in Certain Alaska Waters by Cruise Vessel Operations, 2004 Operating Season Quality Assurance/Quality Control Plan For Sampling and Analysis of Treated Sewage and Graywater From Commercial Passenger Vessels.

*“This document is submitted by Northwest CruiseShip Association to fulfill certain requirements of 33 CFR 159 United States Title 33 Code of Federal Regulations Part 159 and Alaska Statute 46.03.460 – 46.03.490 and 18 AAC 69.*

*Table 2. ANALYTICAL METHODS AND QUALITY CONTROL REQUIREMENTS.*

<i>LAB PARAMETER</i>	<i>METHOD</i>	<i>MDL (mg/L)</i>	<i>REPORTING LEVEL MINIMUM LEVEL (mg/L)</i>	<i>PRECISION (RPD)</i>	<i>ACCURACY (% Recovery)</i>
<i>Chlorine Residual (total/free)</i>	<i>SM 4500 Cl-G</i>	<i>0.10</i>	<i>0.10</i>	<i>N/A</i>	<i>N/A</i>

### EPA Cruise Ship Sampling Program

*We used a pocket colorimeter (Hach Cat. No. 46700-00) for field measurement of free and total chlorine. This procedure is equivalent to Standard Method 4500-Cl G.”*